

Preparation of carbon aerogel by ambient pressure drying and its application in lithium/sulfur battery

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Abstract Formaldehyde, resorcinol, and sodium acetate were used to synthesize the carbon aerogels by ambient pressure drying. The effect of the ratio of resorcinol and sodium acetate for carbon aerogels was researched by scanning electron microscope and Brunauer-Emmett-Teller characterizations. Then the carbon aerogels were applied in synthesizing sulfur/carbon aerogel composites through a melting method, the specific capacity and cycle performance of lithium/sulfur batteries that adopted the prepared composites as cathodes were measured by galvanostatic discharge–charge. X-ray diffraction, conductivity measurement, cyclic voltammetry, and electrochemical impedance spectra tests were also carried out to help explain the electrochemical performance. Finally, the carbon aerogel with the best properties was chosen for the comparative study of replacement of water by acetone as solvent in the preparation of carbon aerogels. According to our study, the carbon aerogel prepared by ambient pressure drying with high electrical conductivity, controllable pore structure, and high specific surface area was proposed to be used for lithium/sulfur batteries, and the key factors to the performance of carbon aerogel/sulfur composites were discussed.

Keywords Carbon aerogel · Carbon aerogel/sulfur compound · Carbon matrix · Charge/discharge · Lithium/sulfur battery

1 Introduction

In order to meet the challenge of global warming and the limited resources, development of new, low-cost, and environmentally friendly energy is more and more essential. The secondary battery is now the most promising renewable storage device, in particular of the lithium-ion battery. However, the specific energy ranges of present lithium-ion batteries cannot meet the increasing demands of electronic devices. In addition, owing to the limitation of crystal structure of the cathode material, further improving the specific energy resulting from li-ion inserting into the cathode material will become difficult. Therefore, developing a new rechargeable battery with high energy density is of considerable technological importance. From this point of view, the use of sulfur as cathode active material has attracted interest because its theoretical specific capacity corresponds to $1,675 \text{ mAh g}^{-1}$, and a lithium sulfur redox couple could generate energy density of $2,600 \text{ Wh kg}^{-1}$ [1]. Combined with other advantages of abundant resources, low-cost, environmentally friendly, and favorable safety, sulfur shows great potential as the cathode material for the next generation of high-performance lithium batteries [2].

Despite its considerable advantages, the Li–S cell is plagued with problems that have hindered its widespread practical realization. It was reported that Li–S cells with liquid electrolytes had critical drawback in the aspects of cycle life, rate capability, and sulfur utilization [3, 4]. Nowadays, there are many researchers focusing on finding appropriate sulfur composites to figure out these serious problems. As for the matrix material, it mainly needs to possess three characters as follows: (i) the electrical conductivity should be well enough because sulfur is an electron insulator; (ii) sulfur should be well dispersed in the matrix to get a high utilization; and (iii) the matrix should

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restrain the polysulfide from dissolving into liquid electrolytes [5, 6]. In recent years, carbon aerogels were mostly researched as super capacitors because of their attractive properties such as high electrical conductivity, controllable pore structure, and relatively high useable surface area [7]. Exactly, these characters make carbon aerogel be an ideal matrix for sulfur composites, while it has been rarely reported in lithium/sulfur system as far as we know.

However, the current method for carbon aerogel synthesis involves a supercritical drying step, which is usually the most critically and costly step in aerogel synthesis [8]. It would be desirable and possible to make aerogels without supercritical drying. Herein, we synthesized carbon aerogels by ambient pressure drying and investigated the effect of the ratio of raw materials on the properties of carbon aerogel product. Then the carbon aerogels were applied in lithium/sulfur batteries to research the electrochemical performance. Furthermore, the carbon aerogel with the best properties was chosen for the comparative study of replacing the water solvent in the gel by acetone [9]. Meanwhile, the factors to the performance of carbon aerogel/sulfur composites in lithium/sulfur batteries were discussed.

2 Experimental

2.1 Materials synthesis

Formaldehyde (F), resorcinol (R), and sodium acetate (C) were weighed in accordance with the molar ratio of 2:1: x ($x = 1/600, 1/400, 1/300, 1/200$ and $1/100$). The corresponding carbon aerogels were denoted as R/C600CA, R/C400CA, R/C300CA, R/C200CA, and R/C100CA. The weighed F, R, and C were mixed with 50 ml distilled water in a beaker with constant stirring. This solution was sealed and cured for 1 day at room temperature, for 1 day at 50 °C, and for an additional day at 90 °C, to get the RF gel. Then the RF gel was dried at 100 °C under ambient pressure. The dried gel was pyrolyzed in a tube furnace under argon atmosphere for 1 h at 300 °C, for 2 h at 600 °C, and for 2 h at 900 °C. In order to investigate the performance of carbon aerogels prepared by acetone as solvent instead of water, one of the gel samples was cut into thin slices before the drying step, then soaked in acetone for 3 days, and the acetone was replaced per 12 h.

The carbon aerogel/sulfur composites were prepared by a melting method for 6 h at 150 °C and for 2 h at 300 °C in a tube furnace under argon atmosphere, with the weight ratio of carbon aerogel and sulfur of 4:6. The corresponding composites were denoted as R/C600CA-S, R/C400CA-S, R/C300CA-S, R/C200CA-S, and R/C100CA-S.

2.2 Materials characterization

Scanning electron microscopy (SEM; SPA400 Seiko Instruments) was used to visualize the morphology and microstructure. The specific surface area, pore volume, and mesopore size distribution of carbon aerogels were analyzed by the Brunauer-Emmett-Teller (BET) by N_2 physisorption on Quanchrome automated surface area & pore size analyzer (Autosorb SI). The XRD patterns were taking place on a PW1730 X-ray diffraction (XRD) using Cu $K\alpha$ radiation. Four-probe Conductivity Analyzer was used to measure the conductivity of the materials.

2.3 Electrochemical measurements

The carbon aerogel/sulfur composite cathode slurry was made by mixing 70 wt% composite with 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) binder in *N*-methyl- ϵ -pyrrolidinone (NMP) solvent. The slurries were spread onto aluminum foil substrates, dried in vacuum at 100 °C for 15 h, and then cut into pieces with diameter of 1.4 cm. The electrolyte was 1 M $LiPF_6$ solution in a mixed solvent of ethylenecarbonate (EC) and dimethyl carbonate (DMC) (EC/DMC = 1:1, v/v), celgard2400 as the separator. Galvanostatic charging/discharging tests were operated in the potential range of 1.0–2.8 V at room temperature with a battery test system (Neware BTS-610). The cyclic voltammetry (CV) tests were performed on a CHI 660C electrochemical workstation, with a voltage range 1.0–2.8 V and a scanning rate of 0.1 mV S^{-1} . Electrochemical impedance spectra (EIS) of the cells were performed using a Zahner IM6 electrochemical workstation, which was carried out in a frequency range between 100 kHz and 10 MHz at potentiostatic signal amplitudes of 5 mV.

3 Results and discussion

3.1 Characterizations of carbon aerogels and composites

The ratio of R and C is a key factor to the preparation of carbon aerogels. After the polycondensation process, a flexible rubber-like RF gel is respectively generated with the R/C ratio of 300, 200, and 100. Additionally, for those three solutions, the speed forming a gel of the R/C100 solution is the fastest and that of the R/C300 solution is the lowest. All of those three RF gels cause evident volume shrinkage after the drying step, and the R/C100 gel presents the strongest volume shrinkage effect. By comparison, the R/C600 gel and the R/C400 gel are all solid and inflexible, and there is no significant volume shrinkage after drying.

The SEM images of those five carbon aerogels at the same magnification are shown in Fig. 1. The R/C600CA, R/C400CA, and R/C300CA are made up by spherical compact particles with the size of about 4.5, 1.5, and 1.0 μm , separately (Fig. 1a–c). A crosslinked network microstructure of R/C200CA formed by particles with the size of about 150 nm is can be seen in Fig. 1d; obviously, abundant mesoporous and macroporous existed in that material. Figure 1e shows that the R/C100CA depicts non-uniform and large-scale particles, with tiny pores. Therefore, we can conclude that with the increase of the amount of catalyst (i.e., with the decrease of the R/C ratio), the particle size is becoming smaller and the cross-linking effect between the particles is getting closer. The non-uniform and large-scale particles of R/C100CA are probably resulting from the rapid agglomeration of small gel particles, which corresponds to the fast speed of forming a gel, as has been mentioned before. Besides, the RF gel with a higher R/C ratio has greater resistance strength against capillary pressure so that the volume shrinkage is less than the gel with a lower R/C ratio after drying [9].

The adsorption isotherms of nitrogen and mesopore size distributions of the carbon aerogels are shown in Fig. 2. The adsorption isotherms of R/C600CA, R/C400CA, and R/C300CA are similar to the type-II (Fig. 2a–c), which corresponds to an adsorption process on the non-porous or macroporous material. The mesopore size distributions illustrate that all of the R/C600CA, R/C400CA, and R/C300CA have a macroporous structure with the pore size of more than 50 nm. The macroporous is related to the large holes between the particles as has been shown in the SEM images of Fig. 1a–c. The adsorption isotherm of R/C200CA is of type-IV and has a clear hysteresis (Fig. 2d). The hysteresis of R/C200CA is of type-H1. The shape of the hysteresis loop is indicative of the type of pores present. This H1 type is often associated with the porous material, consisting of agglomerates or compacts of approximately uniform spheres in a fairly regular array [10]. The pore size of R/C200CA distributes mainly in the region of 5–10 and 20–50, which represents a majority of mesoporous. A typical adsorption isotherm of R/C100CA shown in Fig. 2e can be classified as type-I. This type of adsorption isotherm indicates a wealth of microporous. The pore size of less than 3.5 nm is shown in the pore size distribution, which indicates that the non-uniform and large-scale particles of R/C100CA are provided with abundance of microporous. We can find that the BET characterizations and the SEM images correspond to each other.

Specific surface area and pore volume data measured by the BET method are shown in Table 1. It is evident that the carbon aerogel with the R/C ratio of 200 depicts the highest specific surface area and the largest pore volume. Therefore,

on the basis of the network morphology, the mesoporous microstructure, the high specific surface area, and the large pore volume, R/C200CA is made to be the most probable matrix for the lithium/sulfur battery. The electrochemical performances of the five composites in lithium/sulfur batteries were tested. The capacity and cycle ability behaviors are shown as follows.

Figure 3 depicts initial discharge curves of those five cathodes, R/C600CA-S cathode, R/C400CA-S cathode, R/C300CA-S cathode, R/C200CA-S cathode, and R/C100CA-S cathode, at current density of 100 mA g^{-1} . Obviously, all the discharge curves show one plateau and the plateau of R/C200CA-S cathode is longer and more flat than any other cathode plateaus. Meanwhile, the R/C200CA-S cathode shows the highest initial specific capacity of 1,491 mAh g^{-1} , which means it has a good utilization of sulfur. The R/C300CA-S cathode, the R/C400CA-S cathode, and the R/C600CA-S cathode have an initial specific capacity of 1,186.6, 801, and 579.2 mAh g^{-1} , respectively, while it is only 457.9 mAh g^{-1} for R/C100CA-S cathode.

Cycle performance of those cathodes at various current densities of 100, 200, and 300 mA g^{-1} are represented in Fig. 4. The decline of discharge capacity with the current density increase is ascribed to a high electrochemical resistance at high current. The R/C200CA-S cathode shows the highest capacities during the cycle test, while it is also evident that there is a dramatical attenuation between the initial capacity and the second one. This is probably because the sulfur attached to the surface of particles will react first during the initial discharge process, and then the polysulfide generated from the electrochemical reaction will be dissolved into the electrolyte, which causes the loss of active substances. Afterward the sulfur within the particles will react in the following discharge process. Due to the resistance of the particles and the absorption of pore structure, the amount of polysulfide dissolved into the electrolyte can be greatly reduced; therefore, the cycle stability is improved. As a result, the capacity retention of the R/C200CA-S cathode is about 97 % under the current density of 300 mA g^{-1} . On the contrary, the R/C100CA-S cathode displays the poorest cycle performance. In order to investigate the reasons for the excellent electrochemical performance of the R/C200CA-S cathode, further characterizations were carried out on the R/C200CA-S composite, and the R/C100CA-S composite was chosen for the comparison.

Figure 5 shows the X-ray diffraction patterns of sulfur and the two composites, R/C100CA-S and R/C200CA-S. Compared with the pattern of sulfur, the XRD spectra of R/C100CA-S exhibits the similar trend, the characteristic peaks are sharp and narrow. This indicates that no obvious phase transformation of sulfur occurred during the preparation. In contrast, the XRD pattern of R/C200CA-S

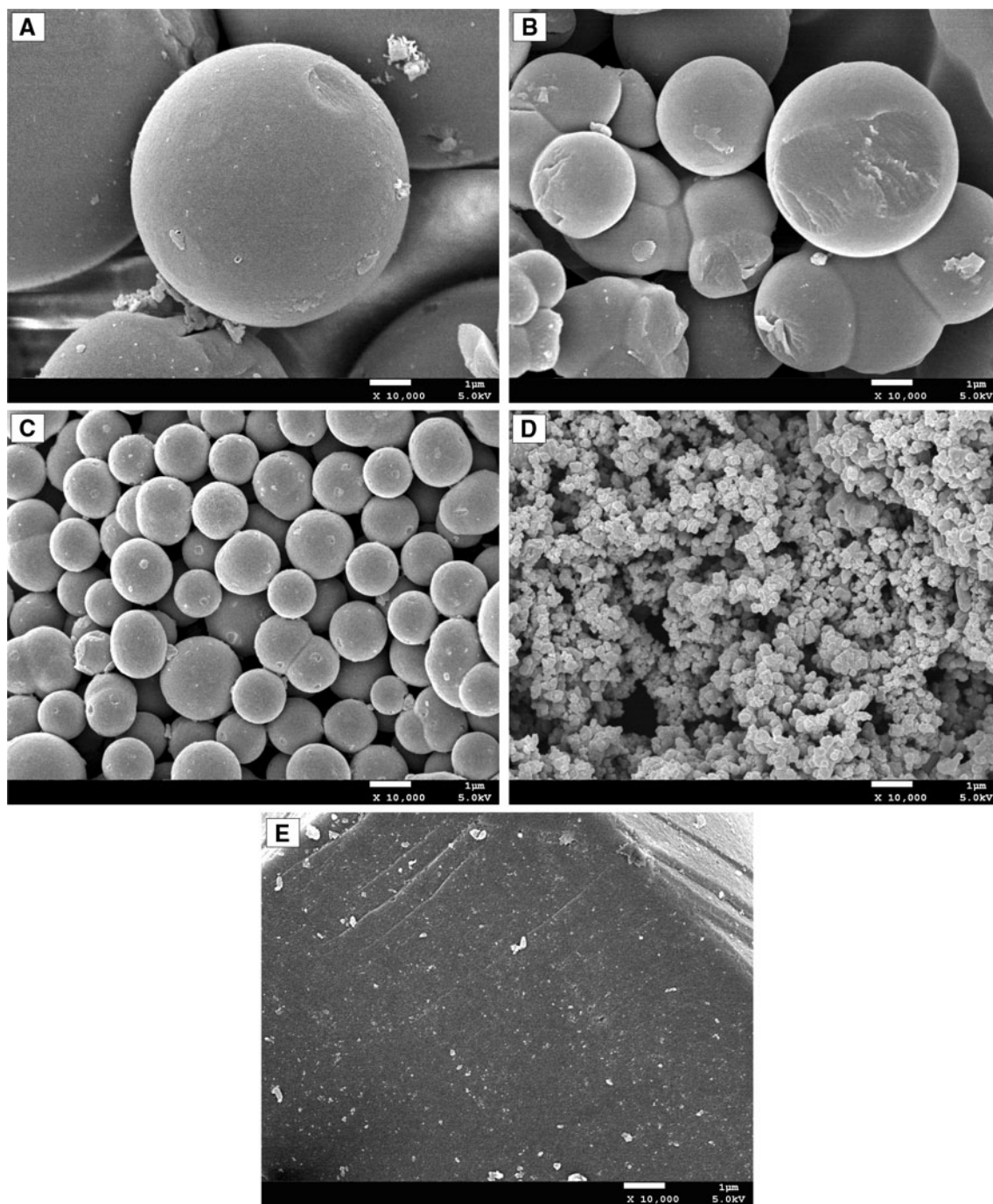


Fig. 1 SEM images of R/C600CA (a), R/C400CA (b), R/C300CA (c), R/C200CA (d), and R/C100CA (e)

presents broad peaks around 24° and 45° , which are attributed to amorphous carbon. Additionally, some of the sulfur characteristic peaks are also observed clearly in the Fig. 5c. Combined with the previous characterizations of R/C200 carbon aerogel, it can be analyzed that sulfur does not only coat on the surface of particles but also diffuse into the inner pores, consequently sulfur in R/C200 carbon aerogel has a better dispersion than in the R/C100 carbon

aerogel. Meanwhile, Four-probe Conductivity Analyzer is used to measure the conductivity of the two composites; the conductivities are of 89.72 S cm^{-1} for R/C200CA-S and 19.26 S cm^{-1} for R/C100CA-S, respectively. A dramatical improvement of conductivity has been obtained in the composites according to the carbon aerogels compared with pure sulfur ($5 \times 10^{-28} \text{ S cm}^{-1}$), especially to R/C200CA-S.

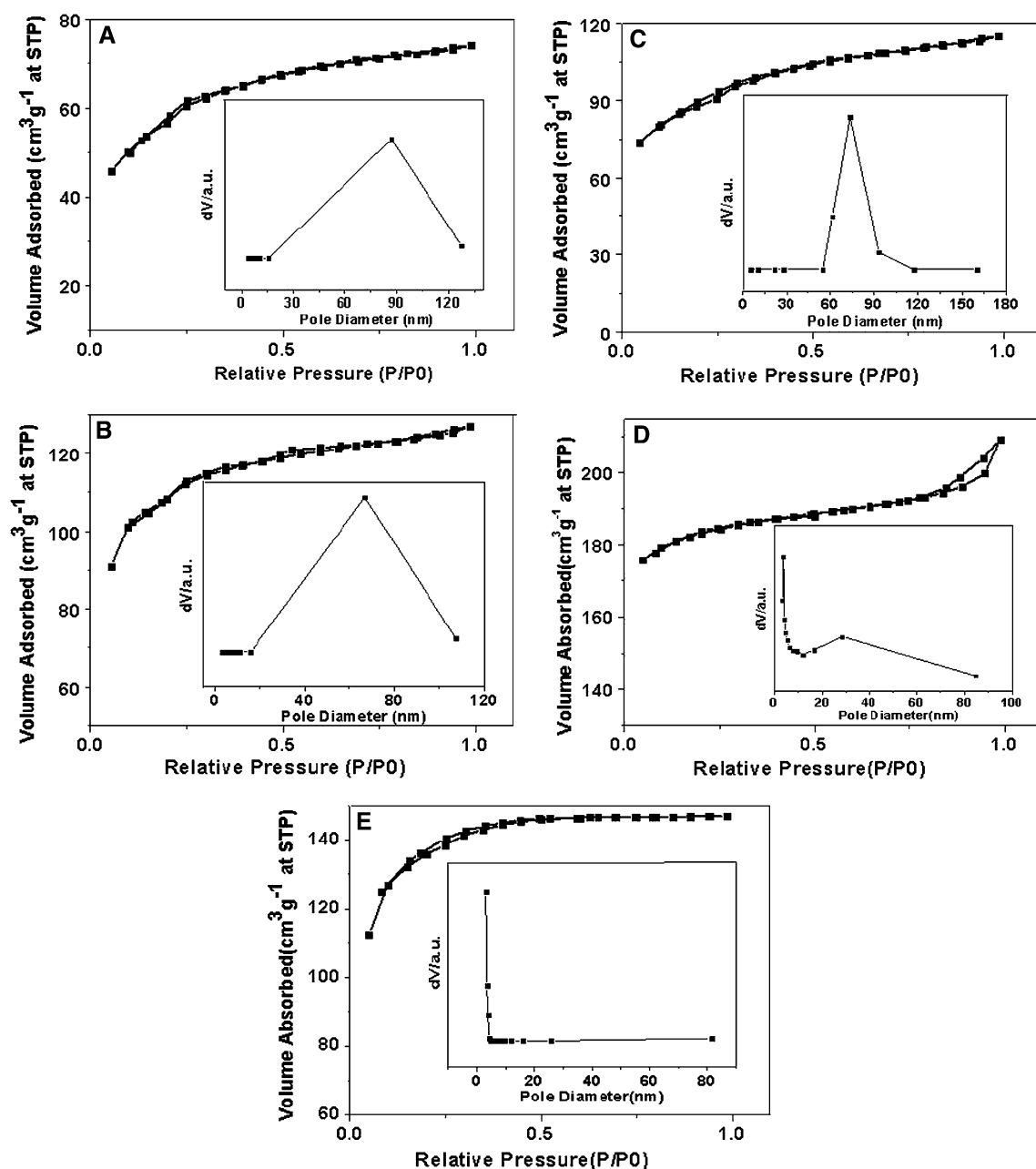


Fig. 2 N_2 adsorption and desorption isotherms and mesopore size distributions of R/C600CA (a), R/C400CA (b), R/C300CA (c), R/C200CA (d), and R/C100CA (e)

The cyclic voltammograms of the cells with those two cathodes were measured at the scan rate of 0.1 mV s^{-1} . As shown in Fig. 6, there exists one anodic peak at about 1.6–1.8 V. The corresponding discharge plateau of this anodic peak is illustrated in Fig. 3. Comparing the peaks of the two cathodes, the anodic peak of R/C200CA-S reveals a narrow and high peak and the smaller potential difference between the peak couple than that of R/C100CA-S cathode. The CV result indicates that the electrochemical polarization of R/C100CA-S is stronger than R/C200CA-S cathode.

Table 1 Specific surface area (S) and pore volume (V) data of the carbon aerogels

Sample	$S \text{ (m}^2 \text{ g}^{-1}\text{)}$	$V \text{ (cm}^3 \text{ g}^{-1}\text{)}$
R/C600CA	302.5	0.1964
R/C400CA	409.3	0.3492
R/C300CA	498.5	0.4417
R/C200CA	613.8	0.6125
R/C100CA	243.6	0.1148

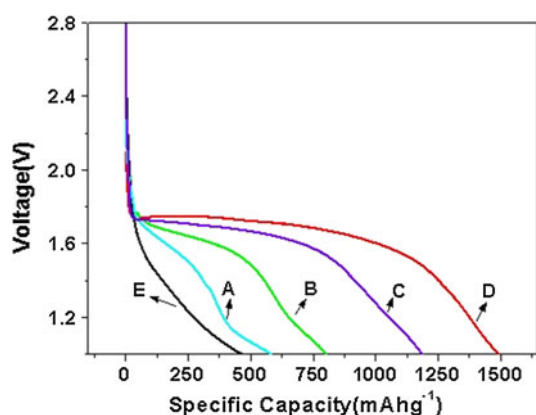


Fig. 3 The initial discharge curves of R/C600CA-S (a), R/C400CA-S (b), R/C300CA-S (c), R/C200CA-S (d), and R/C100CA-S (e) in lithium batteries at current density of 100 Ma g⁻¹

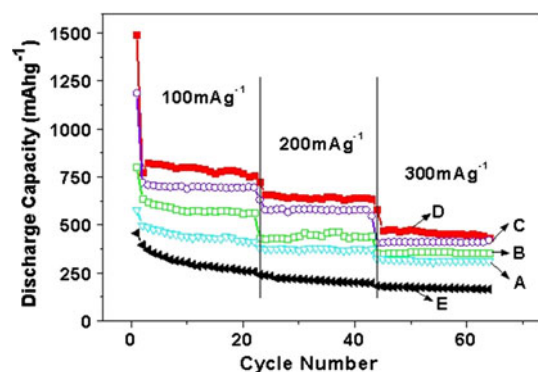


Fig. 4 Cycle performance of R/C600CA-S (a), R/C400CA-S (b), R/C300CA-S (c), R/C200CA-S (d) and R/C100CA-S (e) in lithium batteries at various current densities of 100, 200, and 300 mA g⁻¹

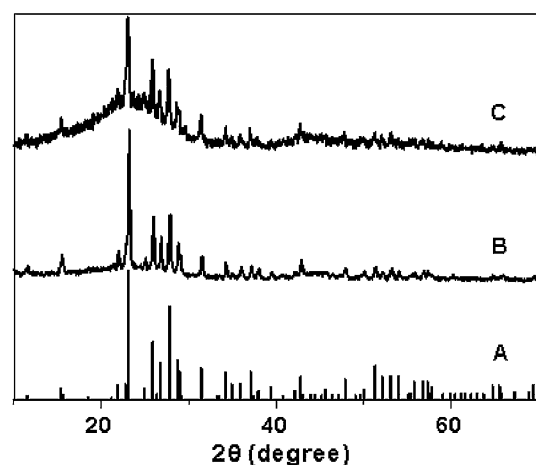


Fig. 5 XRD patterns of sulfur (a), R/C100CA-S (b), and R/C200CA-S (c)

Figure 7 shows EIS plots of the two composite cathodes after one charge/discharge cycle. The intercept between the starting point and the horizontal axis indicates the total resistance of a battery. It is obvious that the total resistance

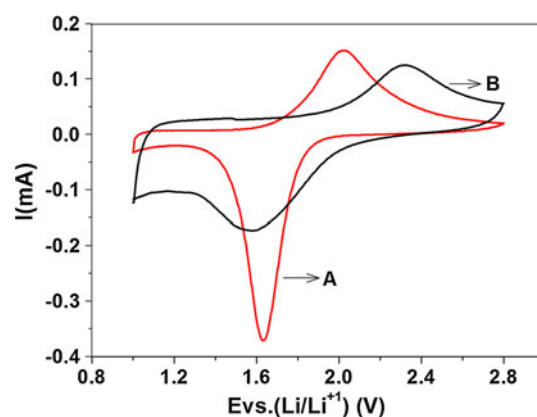


Fig. 6 Cyclic voltammogram of the R/C200CA-S cathode (a) and the R/C100CA-S cathode (b). Scan range: 1.0–2.8 V, and scan rate: 0.1 mV s⁻¹

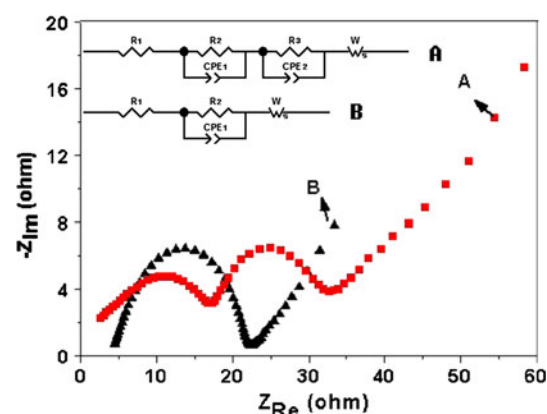


Fig. 7 Impedance plots for electrodes of R/C200CA-S compound (a) and R/C100CA-S compound (b)

of the R/C200CA-S battery is less than that of the R/C100CA-S battery. From the EIS plots we can find that the R/C200CA-S cathode presents two semi-circular arcs, while the R/C100CA-S cathode presents only one. It is reported that the first semi-circular arc of the EIS plots indicates the charge transfer impedance and the second semi-circular arc indicates interfacial impedance [11, 12]. The plots show that the charge transfer impedance of R/C200CA-S cathode is bigger than the R/C100CA-S cathode. Meanwhile, R/C200CA-S cathode exhibits clear interfacial impedance, which indicates that polysulfides are difficult to pass through the interface membrane into the electrolyte. Therefore, it can be concluded that the structure of R/C200CA has a certain restriction effect on the polysulfide from being dissolved into the electrolyte, so that the “shuttle effect” [13] gets weakened. On the contrary, R/C100CA-S cathode does not exhibit interfacial impedance, it can be illustrated that the polysulfides which suffered from a weak restriction are easily dissolved into the electrolyte, so the active materials are losing. From this

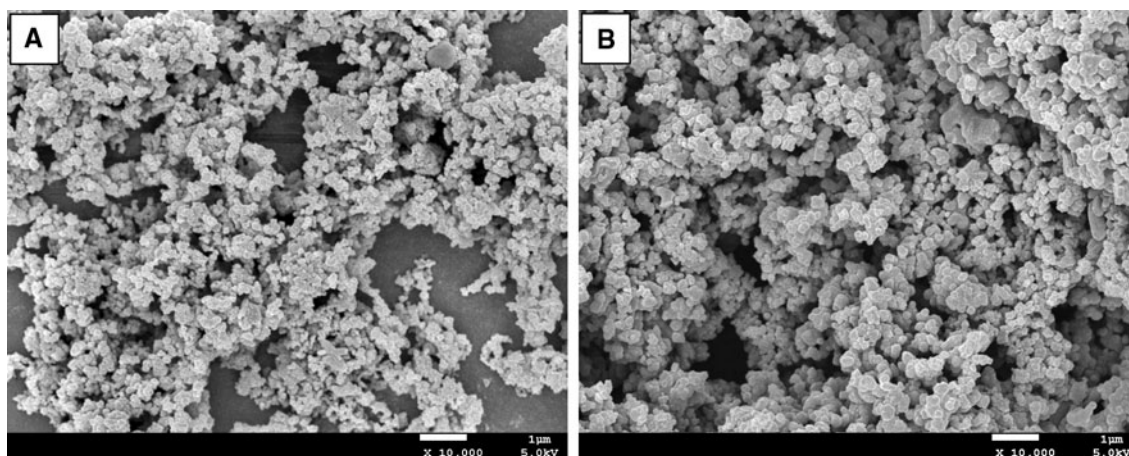


Fig. 8 SEM images of R/C200CA (Acetone) (a) and R/C200CA (b)

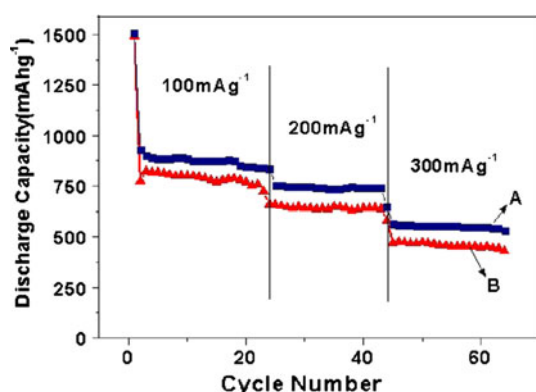


Fig. 9 Cycle performance of R/C200CA(Acetone)-S cathode (b) and R/C200CA-S cathode (b) at various current densities of 100, 200, and 300 mA g⁻¹

point of view, the reason why R/C100CA-S battery shows a poorer electrochemical performance than the R/C200CA-S battery can be explained.

3.2 Effects of replacing the solvent with acetone

In order to investigate the effect of replacing the RF gel solvent with acetone, the R/C200 RF gel was used for the research according to the approach mentioned before. The corresponding carbon aerogel and the composite were denoted as R/C200CA(Acetone) and R/C200CA(Acetone)-S. Figure 8 shows the SEM images of R/C200CA(Acetone) and R/C200CA; we can find that with the same R/C ratio, the morphology of carbon aerogel prepared by replacing the solvent with acetone is similar to the carbon aerogel prepared by the conventional method (R/C200CA). Whereas the specific surface area and pore volume of R/C200CA(Acetone) measured by the BET method is 802.5 m² g⁻¹ and 0.6949 cm³ g⁻¹, both greater than those of R/C200CA (613.8 m² g⁻¹ and 0.6125 cm³ g⁻¹). In the

initial preparation of carbon aerogel, the RF gel is generated from the polycondensation process. Then during the ambient pressure drying, the liquid meniscus within the mesoporous of RF gel will cause capillary pressure before the solvent evaporation. Approximately regard the mesoporous as a cylinder so that the capillary pressure can be expressed as [9]:

$$P = 2\gamma \cos \theta / r$$

The symbols in this equation, γ , θ , and r represent surface tension, interfacial contact angle, and pore radius, respectively. As for water, $\gamma = 72.8 \text{ mN m}^{-1}$, $r = 15 \text{ nm}$, and $\theta = \pi/3$ at ambient pressure; thus the capillary pressure reaches up to 4.9 mpa. While the surface tension of acetone is 26.3 mN m⁻¹, the capillary pressure will be reduced by three times. Therefore, replacing the water solvent by acetone can help relieve the structural shrinkage to a certain extent. Additionally the specific surface area will be increased. As a result, Fig. 9 shows a better electrochemical performance of R/C200CA(Acetone)-S cathode than R/C200CA-S cathode. The capacities are much higher and it is steady at 550 mAh g⁻¹ under the current density of 300 mA g⁻¹. This research further confirms that there is a significant influence of specific surface area and pore volume of the matrix on the electrochemical performance of the composite in the lithium/sulfur cell.

4 Conclusions

In this paper, carbon aerogels were prepared by ambient pressure drying and used as matrix in Li-S battery. The experimental result shows that there is an important influence of R/C ratio on the morphology and microstructure of carbon aerogels: the higher R/C ratio leads to bigger particle size and closer cross-linking effect. The carbon aerogel with the R/C ratio of 200 depicts the mesh

morphology, the mesoporous microstructure, the high specific surface area, and the large pore volume; and its corresponding composite represents the most excellent electrochemical performance in lithium/sulfur cells due to the restriction function on the polysulfides. Additionally, the carbon aerogel prepared by replacing the solvent with acetone has a similar morphology and microstructure to the conventional one, but a higher specific surface area and a larger pore volume, as has been demonstrated in the former, thus its composite cathode in the lithium/sulfur batteries exhibit better electrochemical performance. In conclusion, the morphology, microstructure, specific surface area, and pore volume of the carbon matrix are the key factors impacting on the performance of lithium/sulfur battery. Carbon aerogel with the controlled structure, the high conductivity, and the large specific surface area would probably be widely used for the novel lithium/sulfur battery.

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